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The University of Chicago
Founded by JOHN D. ROCKEFELLER

Stereoisomeric Chlorimido Ketones

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE
SCHOOLS OF ARTS, LITERATURE, AND SCIENCE,
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY.

By Peter P. Peterson

EASTON, PA.:
PRESS OF THE ESCHENBACH PRINTING CO.
1911.

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Stereoisomeric Chlorimido Ketones[1]

In 1803 Stieglitz and Earle[2], in the course of their work on the theory of the "Beckmann Rearrangemedt," discovered the first representatives of a new group of steriosomeric nitrogen derivatives, in which the stereoisomerism depends on the "syn" and "anti" positions of a chlorimide group in chlorimido esters:

$$\begin{array}{ccc} R{-}C{-}OR & \qquad & R{-}C{-}OR \\ \| & & \| \\ NCl & & ClN \end{array}$$

Later Stieglitz and Hale[3] obtained a second pair of such stereoisomeric chlorimido esters and showed under what conditions the labile form can be converted into the stable variety. Finally Hilpert,[4] by preparing five other pairs of stereoisomers and determining the conditions for the transformation of the members of a pair reversibly into each other, established their existence on a sufficiently broad basis. These isomers are interesting, partly because of the simple character of the radical (Cl^+) attached to the nitrogen atom, and partly because of the light they shed on the question of the "Beckmann Rearrangement."[5]

The stereoisomers heretofore prepared, have in all cases been chlorimido esters. They made probable the existence of stereoisomerism also for chlorimido ketones,

$$\begin{array}{ccc} R{-}C{-}R' & \text{and} & R{-}C{-}R' \\ \| & & \| \\ NCl & & ClN \end{array}$$

comparable with the stereoisomeric ketoximes and hydrazones of Hantzsch and Werner and of the former's collaborators. The isolation of such stereoisomers seemed desirable, not only as confirming the conclusions reached in the work on the chlorimido esters, but also because it was thought their prepara-

[1] See a preliminary paper by J. Stieglitz and P. Peterson: Ber. d. chem. Ges., **43**, 782 (1910).

[2] Am. Chem. J., **30**, 399 (1903).

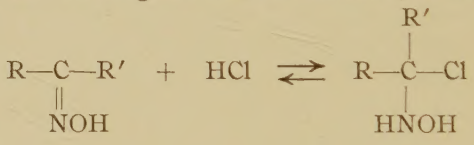
[3] Unpublished results.

[4] Am. Chem. J., **40**, 155 (1908).

[5] See a later paper, to be published by Stieglitz, covering unpublished results with Hale and Eckstein.

tion would settle, experimentally, important questions connected with the "Beckmann Rearrangement." In the rearrangement of ketoximes, R—C(:NOH)R′, under the influence of phosphorus pentachloride, many chemists are inclined to assume[1] the formation of such chlorimides, R—C(:NCl)—R′, as intermediate products, the first products isolated in the reaction being arylimidoacyl chlorides. These are supposed to be formed according to the scheme

According to the theory advanced by Stieglitz, such chlorimides would not be intermediate products; the rearrangement is supposed to be due to the anhydrizing power of phosphorus pentachloride and the other reagents used to accomplish the rearrangement, an intermediate product, containing *univalent* nitrogen, being considered to be the actual substance undergoing the rearrangement. For instance, we would have:[2]



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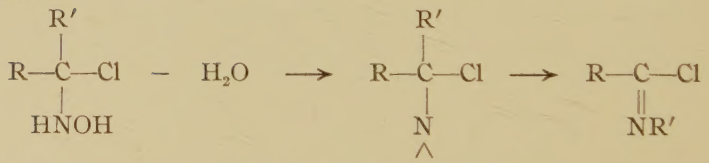
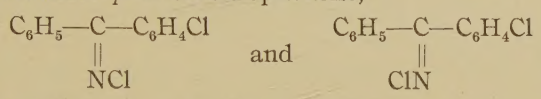


[1] Cf. Hantzsch: Ber. d. chem. Ges., **35,** 3579 (1902).

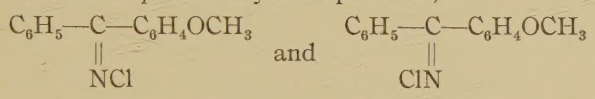
[2] In confirmation of these views, Stieglitz and Reddick have recently found that triphenylmethylhydroxylamine, $(C_6H_5)_3C.NHOH$, whose structure corresponds to that of the assumed intermediate addition product with hydrogen chloride, undergoes the "Beckmann rearrangement" with remarkable ease and smoothness under the influence of a dehydrating agent (phosphorus pentachloride was used). This result is the more noteworthy as it forms a striking contrast to the fact that hitherto all attempts to effect a rearrangement of chlorimidobenzophenone, $(C_6H_5)_2C : NCl$, have been unsuccessful (Stieglitz and Watkins). G. Schroeter has recently (Ber. d. chem. Ges., **44,** 1201 (1911)) brought valuable experimental evidence supporting the above theory. Experiments have been undertaken in this laboratory toward establishing a connection between the rearrangement and the *electrical charges* on the atoms involved. It is thought that, in the final instance, the significance of the rôle of the univalent nitrogen atom will be found to lie in such electrical relations. In a later paper these views will be discussed more elaborately and due consideration given to the confirmative experimental work of Schroeter, as well as to the criticisms of J. Stieglitz, Montagne (*Ibid.*, **43,** 2014 (1910)) and others.

At the suggestion and under the direction of Professor Stieglitz, I undertook the problem of isolating, if possible, such stereoisomeric chlorimido ketones. I have found three pairs of stereoisomers, viz., stereoisomers of:

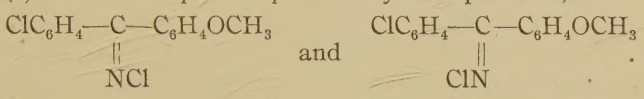
(*a*) Chlorimido-*p*-chlorbenzophenone,



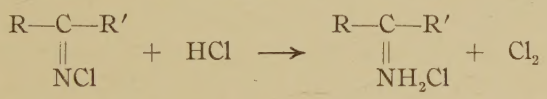
(*b*) Chlorimido-*p*-methoxybenzophenone,



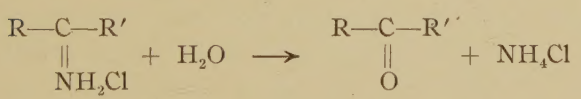
and (*c*) Chlorimido-*p*-chlor-*p*-methoxybenzophenone,



In each case the structural identity of the α and β forms was established by converting each, by dry hydrogen chloride, into the hydrochloride of an imidobenzophenone, which gave with water the same ketone; a mixture of the ketone obtained from the α and that obtained from the β varieties melted at the same point as either separately. The reactions are:



and



That the two forms of a pair are not crystal or physical modifications is shown by the facts that each form has its own characteristic solubility, each form is recovered unchanged from its solutions, from its liquid form, when fused, and from its vapors—even in the presence of added crystals of the other form.[1] Further, each form persists even up to a temperature of 100°, and a mixture of approximately equal quantities of the two forms invariably melts lower than either form alone. One determination of the molecular weight

[1] *Vide* Stieglitz and Earle and Hilpert: *Loc. cit.*

of the higher melting of a pair of stereoisomers was made, namely of the α form of chlorimido-*p*-methoxybenzophenone; the higher melting form should in case of polymerization of either form, be the polymer. The molecular weight determination showed it to have the normal molecular weight for a nonpolymerized body.[1]

The change of one stereoisomer into another was observed only once; the lower melting (β) form of chlorimido *p*-chlorbenzophenone was found, after being kept for three months during a very hot summer, to have become completely converted, spontaneously, into the higher melting, stable or α form. Efforts to induce the same change by artificial means, e. g., by treatment of the two forms with chlorine, were not successful, the stereoisomers being unusually persistent, as compared with the chlorimido esters.[2] It may be recalled here that Hantzsch also found the stereoisomeric hydrazones of these ketones to be extremely stable, resisting transformation into each other by the agents which are usually successful.[3]

The stereoisomeric chlorimido ketones, thus far, have not given the slightest indication of suffering the "Beckmann rearrangement" which they were supposed to undergo so readily by those who had assumed them as intermediate products in the action of phosphorus pentachloride on ketoximes. They can be heated to 100° a short time without undergoing any such rearrangement. It is quite obvious, then, that the view that they form such intermediate products is now wholly untenable.

EXPERIMENTAL PART.

Chlorimidobenzophenone, $(C_6H_5)_2C : NCl$.—The first chlori-

[1] Stieglitz and Earle and Hilpert carried out molecular weight determinations for both stereoisomers of a number of pairs of stereoisomeric chlorimido esters and in every case found the molecular weight of each form normal.

[2] *Vide* Stieglitz, Hale and Hilpert.

[3] By way of the return to the imidohydrochloride of the chlorimido-*p*-chlorbenzophenone, the α form was, by subsequent conversion back into a chlorimide, converted into a mixture of the α and β forms—this process being an aid in the preparation of pure material (the hydrochloride of the imidobenzophenone) for the formation of the chlorimides. As the higher melting α form is always obtained in large excess, the circle enables one to use the material over and over again to accumulate the lower melting β modification. These actions, while proving the structural identity of the stereoisomers, do not accomplish any direct change of one stereoisomer into the other.

mide prepared was that of benzophenone. Here, of course, no stereoisomers were expected, but the work was done for the purpose of developing a good method for preparing chlorimido ketones. Benzophenone was prepared according to the Friedel and Crafts[1] reaction and converted into benzophenone dichloride by means of phosphorus pentachloride according to Kekulé and Franchimont's[2] directions. Benzophenone imidohydrochloride was prepared from the dichloride with the aid of urethane by the method of Hantzsch and Kraft,[3] a yield of forty-two per cent. of the theoretical being obtained. The best yield was obtained when three molecules of urethane were heated with one molecule of benzophenone dichloride. The reaction is a very slow one when carried out at 140°, but the product turns brown, indicating a decomposition, if the temperature is raised much higher. At this temperature the mass gives off gases (carbon dioxide and alkyl chloride) and crystallizes very slowly, and at least three hours are required for completion of the action. Longer heating does not increase the yield.

The chlorimide of benzophenone was prepared from the imidohydrochloride by treatment of the base with hypochlorous acid, much in the same way as the chlorimido esters are prepared. The action is represented by the equation

$$(C_6H_5)_2C : NH + HOCl \longrightarrow (C_6H_5)_2C : NCl + H_2O$$

The hypochlorous acid was prepared from sodium carbonate according to the directions of Erlenmeyer and Lipp.[4] A solution of two equivalents of the acid was prepared and one equivalent of potassium bicarbonate added to it. Then, while the solution was at freezing temperature, the solid imidohydrochloride was added. For instance, 8.5 grams of the hydrochloride was added to a mixture of 4 grams of potassium bicarbonate and of hypochlorous acid (prepared from 17 grams of dry sodium carbonate dissolved in 250 cc. of water and 11.5 grams of chlorine).[5] The solution became milky as

[1] Ann. chim phys., [6] **31,** 510.
[2] Ber. d. chem. Ges., **5,** 909 (1873).
[3] *Ibid.*, **24,** 3516 (1891).
[4] Ann. Chem. (Liebig), **219,** 185 (1883).
[5] Graebe: Ber. d. chem. Ges., **35,** 2750 (1902).

the imidohydrochloride dissolved, and a solid gradually crystallized out. After about ten minutes, during which the mixture was shaken constantly in the freezing bath, chloroform was added to dissolve the crystals. The two layers were separated by means of a separatory funnel, the stoppers of which were carefully greased to prevent any scratching. This precaution was deemed necessary because some nitrogen trichloride was liable to be produced in the reaction and the pungent odor of the mixture indicated its presence.

On evaporation of the chloroform, a yellowish crystalline mass was left. This mass was purified by crystallization from chloroform and ligroin and by recrystallization from warm ligroin. A yield of chlorimide representing seventy per cent. of the theoretical was thus obtained. The melting point of the crystals was 37°. The chlorimidobenzophenone thus obtained, when treated with potassium iodide in acid solution, sets iodine free quantitatively according to the equation

$$(C_6H_5)_2C : NCl + 2HI = (C_6H_5)_2C : NH_2Cl + 2I$$

This was used as a means of analysis, the iodine set free being titrated with sodium thiosulphate.

0.1872 gram substance gave 0.0308 gram chlorine.

	Calculated for $C_{13}H_{10}NCl$	Found
Cl	16.44	16.46

The chlorimide (0.4 gram) was dissolved in 25 cc. of ligroin, and dry hydrogen chloride was passed into the solution; a fine white precipitate resulted which analysis proved to be the regenerated imidohydrochloride.[1] The yield was quantitative. Analysis of it, by the silver nitrate method, gave the following results:

0.0776 gram substance gave 0.0128 gram chlorine.

	Calculated for $C_{13}H_{12}NCl$	Found
Cl	16.30	16.49

Treatment of the imidohydrochloride with hot water gave ben-

[1] *Vide* the equation, page 5.

zophenone quantitatively.[1] That the substance thus obtained was the ketone was proved by the fact that it melted at 46°, the melting point of synthetically prepared benzophenone, and when it was mixed with the synthetic product its melting point was not depressed.

*Hydrochloride of Imido-*p*-chlorbenzophenone,* C_6H_5—C(: NH_2Cl)—C_6H_4Cl.—Chlorimido-*p*-chlorbenzophenone was prepared in the same way as chlorimidobenzophenone, starting from *p*-chlorbenzophenone. This ketone was prepared according to Hantzsch and Kraft's[2] directions, and when treated with phosphorus pentachloride according to Overton's[3] method it gave *p*-chlorbenzophenone dichloride. Fractionation of the dichloride was carried out in a Brühl apparatus, the pure substance distilling at 192° under 12 mm. pressure. A yield of 88 per cent. of the theoretical was thus obtained.

To prepare *p*-chlorbenzophenone imidohydrochloride one molecule of *p*-chlorbenzophenone dichloride was mixed with three molecules of urethane and the whole heated to 140°–160° on the metal bath until the entire mass solidified. This was then extracted four times with benzene to free it from unchanged urethane and *p*-chlorbenzophenone which is formed. Recrystallization, by dissolving the crude residue in chloroform and precipitating with ligroin, gave the pure white hydrochloride. Owing to its difficult solubility in chloroform, it was found impractical to use this method for the purification of large quantities of material. I found that the imidohydrochloride did not need to be purified before conversion into the chlorimide. More nitrogen trichloride was formed, but this did not interfere with the work, and is not dangerous if the stopcocks are kept well greased with vaseline. The chlorimide could then be converted back into the imidohydrochloride quantitatively by the use of hydrogen chloride. This was found to be an easier method of preparing the pure imidochloride than the method of precipitation spoken of above, and it was used exclusively after the first preparation. A yield of 53 per cent. of the theoretical was obtained of the

[1] *Vide* the equation, page 5.

[2] *Loc. cit.*

[3] Ber. d. chem. Ges.; **26,** 28, (1893).

crude material, and this was reduced to 42 per cent. in passing through the chlorimide. Analysis of the pure substance gave the following results:

0.1172 gram substance gave 0.0167 gram Cl, and 0.1224 gram substance gave 0.0175 gram Cl.

	Calculated for $C_{13}H_{11}NCl_2$[1]	Found I	Found II
Ionizable Cl	14.09	14.24	14.30

Stereoisomeric Forms of Chlorimido-p-*chlorbenzophenone*, $C_6H_5—C(=NCl)—C_6H_4Cl$ and $C_6H_5—C(=ClN)—C_6H_4Cl$.—α- and β-*p*-Chlorbenzophenone chlorimide were prepared from *p*-chlorbenzophenone imidohydrochloride by treatment with hypochlorous acid. A solution of two equivalents of hypochlorous acid was prepared as described above and the solid imidohydrochloride added to it. When the crude salt, containing ammonium chloride, was used much effervescence occurred. Great care had to be taken in handling the product, owing to the formation of nitrogen trichloride. No explosions ever did occur, but chemists trying the method must work very cautiously. After the imidohydrochloride was added, the flask was shaken vigorously in the freezing mixture for about ten minutes. The mixture was then extracted with very little chloroform and the chloroform solution drawn off in a separatory funnel. The chloroform was evaporated by a blast of air, a semisolid mass being left. This was extracted with warm ligroin. A solution of a mixture of the two forms of the chlorimide was thus obtained (about 80 per cent. of the theoretical yield). The two forms were separated as follows: Crystals obtained by cooling the ligroin extract were dissolved in as little chloroform as possible and about four volumes of ligroin added. This precipitated a mass of crystals which melted at 101°–102°. Recrystallization from warm ligroin raised their melting point to 104°. This form of the compound is called the α form. It appears in thin plates.

[1] Only the ionizable chlorine is determined, the method used being the titration of the salt with silver nitrate.

The chloroform-ligroin filtrate was then cooled to about —10° for a few minutes. Crystals melting at 46°–48° separated out. On repeated crystallization of this product from ligroin its melting point was finally raised to 55°. This form of the compound is called the β form. It appears as thin prisms or needles. Analysis of the two varieties by the potassium iodide method gave the following results:

0.1592 gram of the α form gave 0.0225 gram active chlorine and 0.1190 gram gave 0.0168 gram active chlorine.

	Calculated[1] for $C_{13}H_9NCl_2$	Found I	Found II
Active Cl	14.18	14.14	14.12

0.1274 gram of the β form gave 0.01817 gram active chlorine and 0.0940 gram gave 0.0136 gram active chlorine.

	Calculated for $C_{13}H_9NCl_2$	Found I[2]	Found II[2]
Active Cl	14.18	14.26	14.45

The identity of the structure of the two compounds was proved by converting them both into the imidohydrochloride and then into the ketone as follows:[3]

Three-tenths gram of the pure α form was dissolved in about 25 cc. of ligroin and dry hydrogen chloride passed into the solution to saturation. The imidohydrochloride was thus precipitated. The ligroin was decanted and the last traces blown off by a blast of air. Then the salt was treated with warm water. This gave 0.223 gram (89 per cent. of the theoretical yield) of the ketone, melting at 75°.5–76°. Mixtures of this substance with the synthetically prepared ketone and with the ketone obtained from the β form melted at the same temperature.

Three-tenths gram of the pure β form was treated in the same way and gave 0.230 gram of the same ketone as was obtained from the α form.

[1] Only one of the two chlorine atoms is determined, it alone being active toward the hydroiodic acid which was used in the analysis.

[2] In the preliminary report by Stieglitz and Peterson, as the result of errors in calculation 14.19 and 13.97 per cent. was reported.

[3] See page 5.

These experiments show conclusively that the substances are not structural isomers and are the same except in the configuration of the radical (: NCl).

The following experiments were carried out to exclude the possibility of crystal isomerism. One-tenth gram of the α form was heated to 120° and cooled slowly. At 85° solidification took place very rapidly. One-tenth gram of the β form was heated to 60°, then cooled to 45° and kept at that temperature for some time. No crystals separated out until inoculated with α or β crystals. The melting point was then found to be 54°; 55° is the melting point of the purest β form. A trace of the β form probably was in the α material and caused crystallization. The melting point shows that the substance persisted in the β form. One-tenth gram of each form was then brought into solution, separately, so that each solution was saturated at 25°. Cooling of the solutions then gave only the crystals from which the solutions were originally made, as melting point determinations proved. The crystals were again brought into solution, the solutions supercooled and inoculated with crystals of the other variety. Again, nothing but the crystals from which the solutions were originally made were obtained, as proved by their melting points and habit.

Hydrochloride of Chlorimido-p-*methoxybenzophenone*, $C_6H_5C(:NH_2Cl)C_6H_4OCH_3$.—*p*-Methoxybenzophenone was prepared according to the method of Gattermann, Ehrhardt, and Maisch.[1] The first preparation was made from anisyl chloride and benzene, but the yield was small. Benzoyl chloride and anisole gave, by the same treatment, almost a quantitative yield. This method was therefore used in subsequent preparations. It was found best to dissolve one equivalent of benzoyl chloride in ten times its volume of carbon disulphide and to add aluminium chloride to the mixture in about the same weight as the benzoyl chloride. A little more than one equivalent of anisole was then allowed to run slowly from a dropping funnel into the mixture. The reaction was complete as soon as all the anisole had been added. The carbon disulphide

[1] Ber. d. chem. Ges., **23**, 1204 (1890).

was then distilled off, the aluminium chloride decomposed with water acidulated with hydrochloric acid, and the ketone extracted with ether. Recrystallization from high-boiling ligroin was the best method found for the purification. The pure substance melted at 62°.

The ketone dichloride was obtained by the Hantzsch and Kraft[1] method, except that it was not purified. It was found that purification was not necessary before treatment with urethane. The excess of phosphorus pentachloride and the phosphorus oxychloride were distilled off in a vacuum at about 100°. The residue was treated directly with urethane. This gave an impure hydrochloride which could be readily purified. For instance, 20 grams of *p*-methoxybenzophenone and 20 grams of phosphorus pentachloride were heated in a flask on a metal bath to 140°–160° for three hours. The phosphorus oxychloride was then distilled off in a vacuum. The residue was treated with 18 grams of urethane and the temperature again raised to 160° for several hours. The viscous mass thus obtained was extracted several times with benzene to remove any urethane, ketone and dichloride. A white solid remained. The crude yield was 17 grams, or 73 per cent. of the theoretical. The substance melted above 170° with decomposition. When treated with warm water it gave a substance melting at 55°–58°, which, when mixed with synthetically prepared ketone (melting at 62°), melted a little higher than before. These facts indicated that the substance was impure imidohydrochloride of *p*-methoxybenzophenone. The hydrochloride was obtained in a pure state by converting the crude salt into the corresponding chlorimide, which by treatment with hydrogen chloride in ligroin solution forms the imidohydrochloride again. The analysis of the salt, purified in this way, gave the following results:

0.2390 gram substance gave 0.0339 gram chlorine.

	Calculated for $C_{14}H_{14}ONCl$	Found
Cl	14.48	14.19

[1] *Loc. cit.*

The salt is decomposed into the ketone (melting at 62°) and ammonium chloride on treatment with water.

Stereoisomeric Chlorimides of p-*Methoxybenzophenone*, $C_6H_5—\underset{\underset{NCl}{\|}}{C}—C_6H_4OCH_3$ and $C_6H_5—\underset{\underset{ClN}{\|}}{C}—C_6H_4OCH_3$.—The chlorimides of *p*-methoxybenzophenone were obtained from the impure imidohydrochloride by treatment with hypochlorous acid. A solution of hypochlorous acid was prepared in the same way as described for the preparation of benzophenone chlorimide, and the solid imidohydrochloride of *p*-methoxybenzophenone was added to the solution. When three equivalents of hypochlorous acid were used the product was gummy and hard to handle. When only two equivalents were used, the product was crystalline and gave a higher yield of the low-melting variety of the chlorimide, the one which is the more difficult to isolate. Use of the pure imidohydrochloride gave a still more satisfactory result. The rapid evaporation of the chloroform used for extracting the chlorimides from the hypochlorous acid solution also seemed to give a larger yield of the low-melting variety. In one preparation 10 grams of imidohydrochloride was treated with the equivalent of two molecules of hypochlorous acid. The chlorimides were extracted with chloroform and the chloroform evaporated rapidly by a blast of air. The mass was fractionated by dissolving it in as little chloroform as possible and reprecipitating part of the solid with about four volumes of ligroin. This gave a substance consisting almost entirely of the α variety. After several precipitations from chloroform by ligroin and recrystallizations from warm ligroin alone, the true melting point of the α-variety was found to be 90°. These crystals were thin, six-sided plates. The first chloroform-ligroin filtrate from the precipitate of the α form was cooled to —10° and the beaker scratched. Fine white crystals came out; they were found to melt at 40°–42°. These crystals were dissolved in ligroin in the proportion of 1 gram of crystals to 25 cc. of ligroin and the solution set in the ice box for two days in a stoppered bottle. One very large asymmetric crystal of the β form and

several flat ones of the α variety appeared and could be easily separated mechanically. The melting point of the large crystal was found to be 54°, which was taken as the true melting point of the β form. A mixture of the two forms melted at 40°, which is far below the melting point of either form alone. Analysis gave the following results:

0.1249 gram of the α form gave 0.0177 gram chlorine and 0.1792 gram gave 0.0254 gram chlorine.

	Calculated for $C_{14}H_{12}ONCl$	Found I	Found II
Cl	14.44	14.15	14.19

0.1363 gram of the β variety gave 0.0198 gram of chlorine.

	Calculated for $C_{14}H_{12}ONCl$	Found
Cl	14.44	14.52

Conversion of the chlorimides back into the imidohydrochloride and the ketone, similar to that carried out with the stereoisomers of chlorimido-*p*-chlorobenzophenone, was effected as follows: 0.335 gram of the α form was dissolved in chloroform and ligroin and dry hydrogen chloride passed into the solution to saturation. A yellow, sticky mass which smelled strongly of chlorine separated out. The filtrate was evaporated and gave but a small residue. Treatment of the mass with warm water dissolved it, and when the solution cooled a white crystalline solid, *p*-methoxybenzophenone, separated out. After about two hours the crystals were collected on a filter and dried on a clay plate. A yield of 0.263 gram of the ketone, or 83 per cent. of the theoretical, was obtained. Its melting point was found to be 59°.5–60°. Then 0.259 gram of the β form was subjected to the same treatment. A yield of 0.200 gram of the same ketone, or 89 per cent. of the theoretical, was obtained. The ketone obtained from the β form, and mixtures of this ketone with the preparation obtained from the α form and with synthetically prepared *p*-methoxybenzophenone, all melted at 59°–60°. There can be no question, therefore, of the identity of the structure of the two chlorimides.

Attempts to convert either variety of the chlorimide directly[1] into the other were made but without success. First 1.5 grams of the substance was heated to 100° for three hours. Its melting point was thereby lowered from 90° to 85°–87°. A mixture of the product with some pure α form melted at 88°–89°. Consequently very little transformation, if any, took place even at 100°. Then 0.1 gram of the β form was heated in the same manner; the melting point of the substance was lowered from 54° to 47°. A very small proportion of α form mixed with the β form lowers the melting point of the latter to 40°. There could have been very little change, therefore, if any, of the β into the α form. Finally 0.1 gram of the substance was heated for three hours in an atmosphere of dry chlorine[2] in a sealed tube. The mass became gummy, and after having been crystallized from chloroform, decomposed slightly at 175° but did not melt. Some transformation must have occurred, but not the transformation into the α form. The investigation of this reaction will be continued.

The molecular weight of the α form was determined by the cryoscopic method: 0.0903 gram substance dissolved in 11.58 grams benzene lowered the freezing point 0°.1675; 0.4791 gram in 11.58 grams benzene lowered the freezing point 0°.835.

	Calculated for $C_{14}H_{12}NOCl$	Found I	Found II
Mol. wt.	242.5	246.8	262.6

The theoretical constant, 53, for the lowering of the freezing point of 100 grams of benzene by one gram molecule of solute was used, as in previous determinations with chlorimido esters. The experimental constant, 49, would give the weights 226.5 and 238.

p-*Chlor*-p-*methoxybenzophenone*, $ClC_6H_4—CO—C_6H_4OCH_3$.—The method used for the preparation of *p*-methoxybenzophenone was also used for the preparation of *p*-chlor-*p*-methoxybenzophenone. Thirty-two grams of dry aluminium chloride

[1] Indirectly the two forms may be converted into each other by treatment with hydrogen chloride and subsequent change of the regenerated hydrochloride of the imidomethoxybenzophenone into the chlorimides by means of hypochlorous acid.

[2] Chlorine effects the reversible change of the labile stereoisomers of the chlorimido esters into the stable forms.

was pulverized in a hot mortar and added to a mixture of 100 cc. of carbon disulphide and 32 grams of freshly distilled *p*-chlorbenzoyl chloride.[1] The mixture was then cooled to 0° and kept at that temperature during the addition of twenty grams of anisole. The anisole was added very slowly, only one or two grams at a time, and the mixture was well shaken between the additions. Hydrogen chloride escaped very regularly. When the action ceased at this temperature, the mixture was allowed to warm up to room temperature. The carbon disulphide was distilled off and a mixture of ice and water, acidulated with hydrochloric acid, was added to the residue to decompose the aluminium chloride. During this operation the flask was kept in an ice-salt mixture. The gummy mass resulting was extracted with benzene, and the solution shaken five times with sodium hydroxide to remove any *p*-chlorbenzoic acid. The benzene was then evaporated and the residue crystallized from hot alcohol as follows: The whole mass was dissolved in the least possible quantity of boiling alcohol and then the solution was cooled. Thirty-two and a half grams of crystals separated out. The filtrate was added to an equal volume of cold water. A further precipitation occurred. This fraction was then crystallized from alcohol. The entire yield was 37 grams, or 82 per cent. of the theoretical. The melting point is 125°. Analysis of the substance gave the following results:

0.2323 gram substance gave 0.5797 gram CO_2 and 0.0980 gram H_2O.

	Calculated for $C_{14}H_{11}O_2Cl$	Found
C	68.18	68.06
H	4.49	4.69

Hydrochloride of Imido - p - *chlor*-p-*methoxybenzophenone*, $ClC_6H_4—C(:NH_2Cl)—C_6H_4OCH_3$.—This was prepared from the ketone as follows: *p*-Chlor-*p*-methoxybenzophenone was heated with one equivalent of phosphorus pentachloride on the metal bath to 160° for three hours. The phosphorus oxychloride was then distilled off in a vacuum at a temperature

[1] This was prepared from Kahlbaum's *p*-chlorbenzoic acid, melting at 237°.

of about 100°. Without further purification this crude product was dissolved in chloroform, and ammonia, dried over sodium hydroxide, run into the solution to saturation. A fine white mass, which was mainly ammonium chloride, separated out. This was filtered off and dry hydrogen chloride run into the filtrate to saturation. A yellowish precipitate was thrown down. The chloroform was decanted and the precipitate washed several times with chloroform and finally with ligroin. It was then dried in a vacuum over paraffin. The substance thus obtained gave low values for chlorine content for the hydrochloride of imido-*p*-chlor-*p*-methoxybenzophenone, but its behavior leaves no doubt that it consists chiefly of this salt, in an impure condition. From 10 grams of *p*-chlor-*p*-methoxybenzophenone 0.5 gram of the crude product was obtained. Water decomposes it into ammonium chloride and *p*-chlor-*p*-methoxybenzophenone (melting point 122°, which was raised somewhat by the admixture of the pure ketone, melting at 125°).

Treatment of the crude salt with hypochlorous acid converts it into the corresponding chlorimide, which is described below. It was expected that the latter would be converted by hydrogen chloride back into the hydrochloride of the imide, but contrary to expectations and to the behavior of other chlorimides, the chlorimide of *p*-chlor-*p*-methoxybenzophenone did not form a *pure* imidohydrochloride when treated with hydrogen chloride. The following analysis was obtained for the crude product prepared by the action of ammonia on the ketone dichloride:

0.2816 gram substance gave 0.0296 gram chlorine.

	Calculated for $C_{14}H_{13}ONCl_2$	Found
Cl	12.57	10.54

The behavior of the salt towards water agrees with the structure assigned to it, and the preparation of pure chlorimides from it (see below) confirms this structure. The preparation of the hydrochloride by this method is considered interesting, as it is the first instance of the formation of an imidohydrochloride from the aromatic ketone dichlorides by the direct

action of ammonia. Hantzsch showed that under the most varied conditions benzophenone dichloride would not form the imido hydrochloride with ammonia, and had to have recourse to the use of urethane with the dichloride in order to prepare the salt. I obtained exactly the same results on repeating Hantzsch's work with benzophenone dichloride.

Stereoisomeric Chlorimides of p-*Chlor*-p-*methoxybenzophenone*, $ClC_6H_4—C(=NCl)—C_6H_4OCH_3$ and $ClC_6H_4—C(=ClN)—C_6H_4OCH_3$.—The crude hydrochloride of imido-*p*-chlor-*p*-methoxybenzophenone (5 grams) obtained in the previous experiment was treated with the equivalent of two molecules of hypochlorous acid in the same way that the other chlorimides were prepared. This gave 3.5 grams of a mixture of α- and β-chlorimides, a yield of 70 per cent. of the theoretical. The product was extracted with about 25 cc. of cold ligroin (40°–60°). The solution was cooled to —20° and gave 1.4 grams of a substance melting at 50°–52°. This was again dissolved in ligroin and the solution set in the ice box in such a manner as to allow a very slow evaporation of the ligroin. Large crystals, mixed with some flat plates of the α variety, came out. The large crystals were recrystallized several times from ligroin before a substance was obtained which gave a sharp melting point, 65°, the highest melting point obtained for this form, the β variety. The residue from the first ligroin extraction was recrystallized from boiling ligroin (boiling at 70°–80°) several times and finally gave the pure α form with a melting point of 94°.5. Melting points of the two varieties and of mixtures of them were taken simultaneously and gave the following results: β form, 64°; α form, 94°; mixture, 50°–52°.

Analysis of the two varieties showed the following: 0.1778 gram of the α form gave 0.0227 gram active chlorine, and 0.1131 gram of the β form gave 0.01442 gram active chlorine.

	Calculated[1] for $C_{14}H_{11}ONCl_2$	Found	
		α	β
Active Cl	12.66	12.75	12.75

[1] Only the chlorine in the (: NCl) group is indicated by the analysis, which was made with the aid of potassium iodide.

The same kind of evidence as was used with the other stereoisomeric chlorimides was brought to exclude crystal and structural isomerism. After melting, each substance crystallizes again in its own characteristic form, even when it has been heated several degrees above the melting point of the higher-melting form. When the substances are mixed with each other the melting point is decidedly depressed, as shown above. And, finally, each substance crystallizes in its own form from a solution of a mixture of the two. These facts exclude crystal isomerism.

The stereoisomeric chlorimidoketones were converted back into the ketone in the usual way in order to exclude the possibility of structural isomerism. The results follow: 0.266 gram of the α form was dissolved in chloroform and the solution saturated with dry hydrogen chloride. This treatment produced a white precipitate. Ligroin was then added to complete the precipitation. The chloroform-ligroin mixture was decanted and the last traces of the solvent blown off in a blast of air. The residual salt was dissolved in hot water and gave 0.216 gram of *p*-chlor-*p*-methoxybenzophenone (melting at 124°–124°.5). This is a yield of 92 per cent. of the theoretical. A mixture of the product with the ketone obtained in the same way from the β form melted at the same point and a mixture with synthetically prepared ketone (melting at 125°) melted at 125°. When 0.173 gram of the β form was treated by the same process 0.134 gram, or 90 per cent. of the theoretical weight of ketone (melting at 125°), was obtained.

Attempts to prepare chlorimido-*p*-nitrobenzophenone and chlorimido-*p*-methoxy-*o*-chlorbenzophenone had to be given up as a result of difficulties experienced in preparing the corresponding imidohydrochlorides of the two ketones. A chlorimide of *p*-methylbenzophenone was prepared but not investigated further when it was found that the lower melting of the two stereoisomers, if present at all, formed an oil difficult to purify. A crystalline compound, presumably the higher melting stereoisomer, was not specially purified and melted between 35° and 45°; it contained 14.62 per cent.

of chlorine, while a compound $CH_3C_6H_4C(:NCl)C_6H_5$ would demand 15 44 per cent. There is no doubt that such a chlorimide may be prepared, but since the main object of this investigation was to isolate well-defined stereoisomeric compounds, the product was not further investigated. The oil, according to the analytical results, was not a pure compound, but contained some chlorimide.

o-*Chlor*-p-*methoxybenzophenone*, $ClC_6H_4.CO.C_6H_4OCH_3$. — In the attempt to prepare *o*-chlor-*p*-methoxybenzophenone chlorimide, *o*-chlor-*p*-methoxybenzophenone was obtained from *o*-chlorbenzoyl chloride and anisole. Since it has not been described in the literature, its preparation will be briefly discussed here. Twenty-five grams of *o*-chlorbenzoyl chloride was dissolved in 100 cc. of carbon disulphide and 25 grams of dry powdered aluminium chloride was added to the solution. The mixture was then cooled in a freezing mixture and the equivalent of one molecule of anisole allowed to drop into it slowly from a dropping funnel. Hydrogen chloride was given off regularly and a crystalline body separated out. The carbon disulphide was then distilled off and the aluminium chloride decomposed by water acidulated with hydrochloric acid. The residue was extracted with ether and the extract well washed with sodium hydroxide to free it from any *o*-benzoyl chloride. The ether was then distilled off and the residue fractionated in a Brühl apparatus at reduced pressure. The pure substance distilled at 250° under 50 mm. pressure. Analysis of it shows the following results:

0.1553 gram substance gave 0.3865 gram CO_2 and 0.0680 gram H_2O.

	Calculated for $C_{14}H_{11}O_2Cl$	Found
C	68.18	67.90
H	4.49	4.90

In conclusion, I wish to express my gratitude to Professor Stieglitz for his kind guidance and for the inspiration he has given me.